ARMY RESEARCH LABORATORY

Simple Computation of the Heat of Formation and Density from Theoretically Predicted Values

by Edward F.C. Byrd

ARL-TR-6206 **September 2012**

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory
Aberdeen Proving Ground, MD 21005

ARL-TR-6206 **September 2012**

Simple Computation of the Heat of Formation and Density from Theoretically Predicted Values

Edward F.C. Byrd
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
September 2012		October 2011 to April 2012

4. TITLE AND SUBTITLE
Simple Computation of the Heat of Formation and Density from Theoretically Predicted Values

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Edward F.C. Byrd

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
ATTN: RDRL-WML-B
Aberdeen Proving Ground, MD 21005

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-6206

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
A novel series of scripts have been written in order to dramatically simplify the computation of the U.S. Army Research Laboratory (ARL)-developed crystalline density and heat of formation prediction tools required for the evaluation of performance properties for notional energetic materials. Previously, obtaining these predicted values entailed 7–11 steps consisting of construction of various input files, transcribing data from one output file into the input file of another code, submission and monitoring of calculations to the HPC supercomputers, and error-checking routines all prior to final results being generated. With the advent of the recently developed scripts, a synthetic chemist who is not an expert in computational computing can simply construct the molecular geometry and submit one input file, with the scripts performing all the required file construction, submissions, error checking, and data manipulation. This paper outlines the steps required to gain access to the ARL scripts and supercomputers, as well as information on how to properly use the scripts and support programs.

15. SUBJECT TERMS
Computational toolbox, script, crystalline density, heat of formation

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Edward F.C. Byrd
Unclassified	Unclassified	Unclassified	UU	48	19b. TELEPHONE NUMBER (*Include area code*) (410) 306-0729

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures

List of Tables

Acknowledgments

Dr. Betsy Rice and Jennifer J. Hare are acknowledged for their efforts in the original coding of the neutral heat of formation and EDAT tools, respectively. Dr James Ianni (Applications Engineer with Lockheed-Martin, Contractor to the U.S. Army Research Laboratory [ARL] DoD Supercomputing Resource Center [DSRC]) is acknowledged for his *gsubmit* script, initially written for the ARL DSRC. Dr William Sherrill (Energetic Materials Branch, WMRD, ARL) is acknowledged for providing helpful input during beta testing. All computations were performed at the ARL DSRC, Aberdeen Proving Ground (APG), MD.

INTENTIONALLY LEFT BLANK.

1. Introduction

In recent years, the U.S. Army Research Laboratory (ARL) researchers have achieved significant successes in developing theoretical models capable of predicting performance properties, such as heats of formation (*1, 2*) and densities (*3*) of energetic materials (EM). These models allow synthetic and formulation chemists to safely and quickly screen candidate materials in order to focus efforts only on the most promising compounds.

ARL researchers Edward F.C. Byrd and Betsy M. Rice have established correlations of quantum mechanically derived properties with heats of formation and crystalline densities for both neutral and ionic solid energetic materials. These two properties are critical elements in predicting the detonation and propulsion properties of a material. As the crystal structure of a novel material may not be known, each of the correlations requires quantum mechanical data solely from single molecules and not any from bulk material. However, the current codes used to produce the required information are cumbersome to use and prone to failure unless strict formatting rules are followed.

In this report, a brief summary of the methodologies employed will be presented, followed by the current state of the codes used to generate the final results. The final goals of the recently developed tools designed to eliminate user error will be delineated and subsequently expanded upon in further sections. Finally, sample inputs and outputs will be presented.

1.1 Neutral Heat of Formation

Initially developed in 2006 (*1*), the neutral heat of formation prediction tool uses Hess's law (equation 1) (*4*) to combine an atomic or group equivalency equation for the gas phase heat of formation (equation 2) coupled with an equation correlating properties of the electronic density for the heats of vaporization (equation 3) or sublimation (equation 4).

$$\Delta H^\circ_{f\,(liquid/sold)} = \Delta H^\circ_{f\,(g)} - \Delta H_{vap/sub} \quad (1)$$

$$\Delta H^\circ_{f\,(g)} = E - \Sigma\, n_j \varepsilon_j \quad (2)$$

$$\Delta H_{vap} = a(SA)^{1/2} + b(\sigma^2_{tot}\nu)^{1/2} + c \quad (3)$$

$$\Delta H_{sub} = a(SA)^2 + b(\sigma^2_{tot}\nu)^{1/2} + c \quad (4)$$

In equation 2, E is the quantum mechanically determined electronic energy, n_j is either the number of atom or group types j contained in the neutral molecule, and ε_j is either the atom or group equivalent energy of atom/group j. These equivalent energies were determined through the fitting of experiment gas phase heats of formation [$\Delta H^\circ_{f\,(g)}$] to quantum mechanically computed energies E.

Equations 3 and 4 use statistics derived from the electrostatic surface potential (ESP), previously demonstrated by Politzer et al. (*5*–*7*) to correlate to heats of vaporization and sublimation. Following the conventions lay down by Politzer et al. (*8*) and Rice et al. (*9*), the definitions of these electrostatic properties are global properties across the 0.001 electron/bohr^3 isosurface of electronic density. The electrostatic potential V is defined as:

$$V(\mathbf{r}) = \sum_i \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')\mathrm{d}\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|}, \tag{5}$$

where Z_i and $\mathbf{R}_i$ represent the charge and position of atom i, and $p(\mathbf{r})$ is the electronic density. The statistical tools developed by Politzer et al. (*8*, *10*) used in equations 3 and 4 are the surface area (SA), the variance of electrostatic surface potential (σ^2), and the balance parameter (ν). These are defined as:

$$\Sigma^x = \frac{1}{n}\sum_{i=1}^{n} V^x(r_i) \tag{6}$$

$$\sigma_x^2 = \frac{1}{n}\sum_{i=1}^{n} |V^x(r_i) - \Sigma^x|^2 \tag{7}$$

$$\sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2 \tag{8}$$

$$\nu = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{tot}^2]^2}, \tag{9}$$

where $V(r_i)$ is the value of the ESP at r_i and Σ is the average electrostatic surface potential (x is either the positive (+) or negative (–) portion of the ESP). The surface area is the surface area of the 0.001 electron/bohr^3 isosurface of the electron density of the molecule, σ^2_{tot} is a measure of the variability of electronic potential on the surface, and ν is the degree of balance between the positive and negative charges on the isosurface. Equations 3 and 4 each come with a different set of fitted a, b, and c parameters.

As illustrated in reference 1, this methodology enjoys considerable accuracy, with the root mean square error (rms) for the solid phase heat of formation under 6 kcal/mol (figure 1). Table 1 reveals the excellent agreement with experimental gas-, liquid-, and solid-phase heats of formation this methodology exhibits, with the group equivalent energies yielding slightly better solid-phase heats of formation over the atom equivalent.

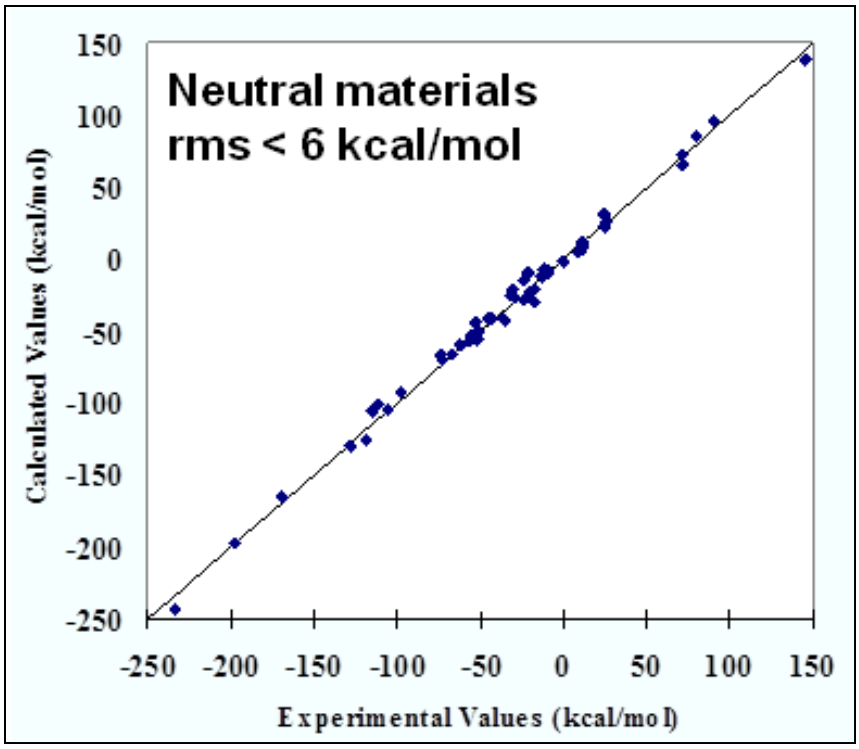


Figure 1. Accuracy of the neutral solid phase heat of formation tool (reference 1).

Table 1. Root mean square errors and maximum deviations for the gas, liquid and solid phase heat of formation for neutral materials using the B3LYP/6-311++G(2df,2p) energies (reference 1).

	Atom Equivalent		Group Equivalent	
	rms error	**max error**	**rms error**	**max error**
$\Delta H°_{f(g)}$	2.8	5.4	3.2	6.5
$\Delta H°_{f(l)}$	3.1	7.2	3.2	7.4
$\Delta H°_{f(s)}$	6.0	16.7	5.6	12.2

The current methodology required to compute the neutral solid-phase heat of formation for a notional material is as follows:

1. Build the notional molecule.
2. Compute the optimal geometry using the B3LYP spin-restricted Kohn-Sham density functional theory (KS-DFT) (*11*) with the 6-31G* Pople gaussian basis set (*12*), currently done using the Gaussian09 program package (*13*).
3. Check whether the final geometry is a stable minimum or if it is a transition state (determine from an additional Gaussian09 vibrational frequency calculation).
4. Compute the electronic energy of the optimized geometry (step 2) using the B3LYP density functional theory with the 6-311++G(2df,2p) Pople gaussian basis set (*12*).

5. Build the cube and pot files from the wavefunction data using the Gaussian *formchk* tool.
6. Run the ARL EDAT tool, developed for ARL researchers by Jennifer Hare, to determine the molecular surface area along with the various required Politzer parameters.
7. Determine the number of atom/group types for the notional molecule.
8. Plug the aforementioned computed parameters into the neutral heat of formation formula.

This is a fairly lengthy process and is prone to transcription errors. However, all this is required to generate just one of the potentially desired properties, and this procedure is not the most complicated presented herein.

1.2 Crystalline Density

Developed in 2007 (*3*), the crystalline density predictor methodology correlates the quantum mechanically derived electronic density volume of the molecular unit to the crystalline density. Similarly to the neutral heat of formation correlation, this correlation also has exhibited significant success in predicting the crystal density. As discussed in reference 3, it was determined that the crystal density correlated very well with the quantum mechanically derived molecular volume. Rice *et al.* found that the 0.001 electron/bohr^3 isosurface of the electron density of the isolated molecule (the same isosurface as used for the neutral heat of formation tool) encapsulated the molecular volume and yielded an excellent correlation to density (figure 2).

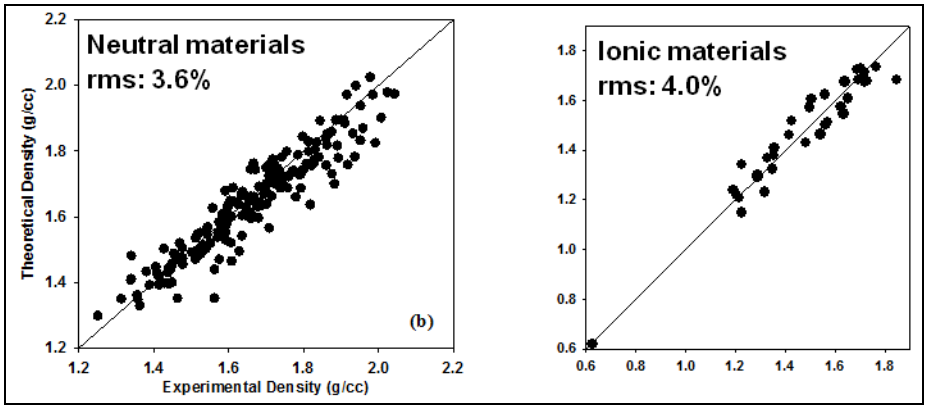


Figure 2. Accuracy of the crystalline density prediction tool. The image on the left is for neutral species, while the image on the right is for ionic compounds. Associated root mean square errors are presented (reference 3).

The derived correlation contains no fitted parameters, and simply requires the quantum mechanically derived molecular volume and the molecular mass (equation 10).

$$\rho_{crystal} = (\text{total molecular mass}) / (\text{total molecular volume}) \quad (10)$$

While it is simple to determine the molecular volume for neutral species (as there is only one molecule), calculating the formula unit volumes of ionic systems can be difficult if no *a priori* knowledge of the crystal structure exists. As a multi-component system (e.g., ionic systems) can have a near infinite combination of potential relative separations and orientations of the components in the formula unit, it can be problematic to determine the most probable arrangement that most closely corresponds to the crystalline phase without this advanced knowledge. Any attempt to sample the phase space of possible configurations has no guarantee of properly capturing the correct experimental crystal structure. In order to avoid testing multiple different configurations, one can assume additivity of the individual components to define formula unit volumes (*14–16*).

Assuming an additive approach implies that the volume of the formula unit M_pX_q of an ionic crystal is simply the sum of the volumes of the ions contained in the formula unit:

$$\text{Volume} = pV_{M+} + qV_{X-}, \tag{11}$$

with M denoting the cation and X the anion. For formula units containing more than two components (such as when solvent molecules are present in the crystal lattice), the additional molecules are also included in the total volume:

$$\text{Volume} = pV_{M+} + qV_{X-} + rV_{\text{solvent}}, \tag{12}$$

where r is the number of solvent (or additional) molecules in the formula unit.

Rice et al. determined that for ionic systems, errors were introduced with increasing hydrogen content, such that there was a linear correlation with the number of hydrogen atoms in an ion and the error in the predicted volume. It was concluded this error was due to overly long X-H (X = N, C) bonds, as predicted by the quantum mechanical method employed. Therefore, a correction to the molecular volume was established in order to reduce the error in the initial quantum mechanical volume:

$$V_{\text{corrected}} = V_{\text{uncorrected}} - [0.6763 + 0.9418\ (\#\ H_{\text{ion}})] \tag{13}$$

The current methodology for calculating the crystalline density for a notional material is as follows:

1. Build the notional molecule.
2. Compute the optimal geometry using the B3LYP KS-DFT with the 6-31G** Pople gaussian basis set (*12*).
3. Check whether the final geometry is a stable minimum or if it is a transition state (determine from an additional vibrational frequency calculation).
4. Build the cube and pot files from the wavefunction data using the Gaussian *formchk* tool.

5. Run the ARL EDAT tool to determine the molecular volume and correct for number of hydrogens.
6. Determine the molecular mass.
7. Plug the computed parameters into the density formula.

1.3 Ionic Heat of Formation

The ionic heat of formation tool was developed in 2009 (*2*) and followed a similar methodology as that for the neutral heat of formation correlation. However, for ionic materials, one cannot use the heat of sublimation coupled with the gas phase heat of formation (as in equation 1), as the intermolecular forces binding the ions together are entirely different than those forces found in neutral materials. The methodology employed, a modified form of the Born-Fajans-Haber cycle (*4*), is formulaically similar to equation 1:

$$M_{(g)} + X_{(g)} \xrightarrow{IE,\,EA} M^{+}_{(g)} + X^{-}_{(g)} \xrightarrow{\Delta H^{\circ}_{Lattice}} M^{+}X^{-}_{solid}, \tag{14}$$

where instead of performing the full cycle (equation 14), the gas phase heats of formation are determined directly for the ions, without ever computing any information on the neutral precursor species (equation 15).

$$M^{+}_{(g)} + X^{-}_{(g)} \xrightarrow{\Delta H^{\circ}_{Lattice}} M^{+}X^{-}_{solid} \tag{15}$$

While the gas phase heats of formation are computed quantum mechanically, the lattice enthalpy ($\Delta H^{\circ}_{Lattice}$) is calculated from the lattice potential energy (U_{pot}), a measurement of the binding energy of the ionic crystal (*17*):

$$\Delta H^{\circ}_{Lattice} = U_{pot}(M^{+}_{p}X^{-}_{q}) + [p(n_{M^{+}}/2 - 2) + q(n_{X^{-}}/2 - 2)]RT, \tag{16}$$

where $n_{M^{+}}$ and $n_{X^{-}}$ depend on whether the ions are monatomic, linear polyatomic, or non-linear polyatomic species, and T is 298 K. As discussed in reference 2, the calculation of the lattice potential energy will use either the Jenkins model (*14, 18, 19*) or the Gutowski model (*20*), which is applicable only for 1:1 salts. Both the Jenkins and Gutowski models correlate the molecular volume to the lattice enthalpy:

$$U_{pot} = 2I\left[\frac{\alpha}{\sqrt[3]{V}} + \beta\right], \tag{17}$$

where I is the ionic strength, V is the volume, and α and β are empirically derived parameters (these differ between the Jenkins and Gutowski methods). Please note that the hydrogen-corrected molecular volumes are used when computing the molecular volume (equation 13).

As illustrated in table 2, the methodologies do reasonably well for predicting the solid-phase heats of formation for ionic materials. The errors are larger than those observed for the neutral heat of formation tool; however, one must note that the binding energies for ionic materials span a much larger range (~100 kcal/mol) than those usually seen for neutral materials (~10 kcal/mol). While marginally better results can be obtained for non-1:1 salts, assuming one had knowledge of the crystal structure, the Jenkins methodology allows for a completely predictive tool for the determination of solid-phase heats of formation of molecular energetic salts without requiring this information. Surprisingly, the Gutowski method for 1:1 salts yielded the best overall results (*2*).

Table 2. Solid phase heats of formation for ionic materials predicted using various methods to calculate component $\Delta H°_{f(g)}$ and $\mathbf{\Delta H^{\circ}_{Lattice}}$ (reference 2).

Theoretical Method $\Delta H°_{f(g)} + \Delta H°_{Lattice}$	**unsigned mean error (kcal/mol)**	**rms error (kcal/mol)**
1:1, 2:1, 2:2 salts		
G3MP2(B3LYP) + Jenkins	29.7	36.6
1:1 salts		
G3MP2(B3LYP) + Gutowski	19.1	24.0
G3MP2(B3LYP) + Jenkins	24.4	28.0

The current methodology for calculating the ionic heat of formation for a notional material is as follows:

1. Build each of the components (subunits) in the notional molecular system.
2. Compute the G3MP2(B3LYP) (*21*) gas-phase energies for each subunit.
3. Check whether the final geometries are stable minima or if they are a transition state (determined from the vibrational frequency calculation included in the G3MP2(B3LYP) calculation).
4. Compute the optimal geometry using the B3LYP KS-DFT with the 6-31G** Pople gaussian basis set for each subunit.
5. Check whether the geometries computed with B3LYP/6-31G** are stable minima or if they are transition states (determine from an additional vibrational frequency calculation).
6. Build the cube and pot files from all the wavefunction data using the Gaussian *formchk* tool.
7. Run the ARL EDAT tool to determine the molecular volume of each of the B3LYP/6-31G** structures and correct for hydrogen.
8. Compute the lattice potential from the total system volume using either the Jenkins or Gutowski methodology (dependent on whether the system is a 1:1 salt).

9. Compute the lattice energy from the lattice potential.
10. Compute the total gas-phase heat of formation from the G3MP2(B3LYP) values.
11. Calculate final total solid-phase heat of formation from gas-phase energies and lattice energy.

1.4 Design Goal

As illustrated in the previous sections, the current state of the tools requires an elaborate series of calculations to be performed in a specific order. Unmentioned are the idiosyncrasies inherent in the in-house codes used to compute the required information from the Gaussian output files. There are several issues with the current toolset:

1. Tools are not coupled; i.e., must perform distinct calculations for each property separately.
2. Not "push button" ready; i.e., significant effort required prior to even generating necessary initial Gaussian data.
3. Require extremely format specific inputs. For example, an ARL researcher discovered that being off by a single space or carriage return caused immediate failure.
4. In general, the overall process is tedious and rife for failure, especially for the non-expert user (as can be expected from a series of codes built up piecemeal in order to solve specific issues).

The final design goal of any solution designed to address each of these issues would need to have:

1. A simple input structure, such as:
   (a) *x y z* coordinates and atom type (C, H, N, etc.);
   (b) a single line of information per molecule in the overall system (e.g., charge of ionic partners, number of saturated carbons, etc.); and
   (c) as freeform an input as possible, limiting possible sources of failure due to formatting issues.
2. A means of monitoring all required calculations, limiting user input to an initial input structure, and receiving the final computed results.
3. A coupled procedure, where the researcher need only submit one job.

Each of these needs has successfully been addressed and shall be expounded upon in the following section.

2. Method of Solution

2.1 Code

Three *bash* scripts have been written to address the previously listed issues:

1. One main script that drives the other scripts, as well as submits the required Gaussian calculations and monitors the queues (master_densheat.s)
2. A script to build the required Gaussian input files (gbuild.s)
    a. For density calculations, the script will build a file called *filename*_density.com if the molecule is a neutral or *filename*_ **[ion]_[number]**_density.com for ionic species (where **[ion]**=*cation*, *anion*, or *neutral* and **[number]** is the running count of that ion type (one through *n*)).
    b. For heat of formation calculations, the script will build a file called *filename*_heat.com if the molecule is a neutral or *filename*_ **[ion]_[number]**_heat.com for ionic species (where **[ion]**=*cation*, *anion*, or *neutral* and **[number]** is the running count of that ion type (one through *n*)).
3. A script to construct the data needed to determine the heats of formation and/or crystalline densities and subsequently calculating said properties (arl_densheat.s)

Given a properly formatted input file, the scripts will analyze the input file and:

- Load the relevant modules (master_densheat.s, arl_densheat.s);
- Determine appropriate format needed and build the required Gaussian input files (gbuild.s);
- Submit the built input files and monitor the PBS queue to determine when calculations are complete (master_densheat.s);
- Copy the required Gaussian output files from the scratch directory to the working directory (master_densheat.s);
- Generate the required Gaussian utility *formchk* .cube and .pot files (arl_densheat.s);
- Run the EDAT tool in order to generate required Politzer statistics (arl_densheat.s);
- Gather required data from all generated files (e.g., surface areas, energies, volumes, etc.) (arl_densheat.s); and
- Compute requested heats of formation or densities (arl_densheat.s).

The scripts also perform a limited series of error checking:

- Checks that for optimized structures, all frequencies are real (i.e., the structure is not a transition state structure, but rather a minima); if not, the script will stop and will print an error message in the *arl_heat_density.err* error file. (master_densheat.s)
- Checks that the required Gaussian outputs do not already exist (the .chk and .out files), and if they do, will not resubmit these Gaussian calculations. Note that if modifications were made to the .dat input file, it is necessary to delete previous .chk and .out files remaining in the working directory. (master_densheat.s)
- For ionic systems, scripts check the total charge is neutral (original tools were not developed for non-net-neutral ionic systems); if not, the script will halt. (master_densheat.s)
- Checks that the Gaussian calculations ran successfully to completion. An error message will be printed in the *arl_heat_density.err* error file if Gaussian failed to complete. (arl_densheat.s)
- For neutral calculations, the script will check that the number of atom types listed in the first line (e.g., number of carbons equals C + C' atom types) correspond to the number of atoms in the Cartesian coordinates. Currently, there is no error check to determine if the number of group types is correct (e.g., C-NO_2,O-NO_2, etc.) If there is a disagreement, the script will halt.

For large molecular systems, an additional master script is available (*large_master_densheat.s*), which acts exactly the same as the standard *master_densheat.s* script with the notable exception of requesting 64 cores and 96 h of queue for use by the Gaussian09 code. Even larger amounts of CPU time and a larger number of cores can be requested through personal modification of a local copy of the script or by request.

2.2 Gaining Access to Required Codes

The ARL scripts are located on the ARL DSRC machine "Harold," with the host name used to log on is "harold.arl.hpc.mil." The directory the scripts are located in is "/usr/people/ebyrd/bin/", which can be aliased if so desired.

In order to use these scripts, prospective users must have access to the ARL DSRC, as well as access to the Gaussian software package. Access to the ARL DSRC can be obtained through the following route (current as of April 2012, subject to change):

1. Go to the Portal to the Information Environment at https://ieapp.erdc.hpc.mil/info/kerberosValidate.jsp
2. At the bottom of the grey box in the middle, click on "Request login account".
3. Click on "Apply for an IE Account" and fill out the required information. The required Kerberos Realm is "HPCMP.HPC.MIL" for US government employees or for those who

intend to get a NAC. For foreign nationals or others who do not want a NAC, access can only be obtained for the Open Systems, and in that case, the Kerberos Realm would be ARSC.EDU. Plans are in place to transition these scripts to the Open Resource System.

4. Select the organization ID "ARLAP".
5. The rest of the questionnaire is self-explanatory and should be completed.
6. Next, go back to https://ieapp.erdc.hpc.mil/info/kerberosValidate.jsp
7. At the top right-hand corner, click on "IAA training." Complete the training, and print out and sign the certificate, and either FAX or scan/email to the ARL S/AAA (Service/Agency Approval Authorities) (Dr Betsy Rice is alternative S/AAA and will accept certificates).

To obtain access to Gaussian, contact the CCAC (Consolidated Customer Assistance Center) (http://www.ccac.hpc.mil/) and request access on the appropriate DSRC (currently ARL) by emailing the help desk at Help@ccac.hpc.mil.

Prior to running the scripts for the first time, it is advised to test that access has, indeed, been granted for all required codes. This is only required as a test to determine if proper access has been granted. It is ***not*** required to do this each time prior to using the script.

To test if proper access has been granted, at the prompt (denoted ">>" in the text) type the following commands:

>>module load g09_c01
>>which g09

where the g09_c01 above is g-zero-nine-underscore-c-zero-one. The **which** command should return something other than "g09: Command not found." Subsequently type the following commands:

>>module use /usr/cta/CSE_MSRM_ATOMISTIC/modules
>>module load cseinit-msrm-atomistic cse-msrm/atomistic/edat/latest
>>which edat

where the **which** command should return something other than "edat: Command not found." If either of the two commands fails, please contact the CCAC help desk.

2.3 Usage

The ARL scripts require only one input file per molecular system (referred to as *filename*.dat in the text). The file name must end in ".dat" and contain no other periods or special characters aside from "-" and "_", which are acceptable. Multiple molecules can be submitted at one time.

>> /usr/people/ebyrd/bin/master_densheat.s *filename1*.dat *filename2*.dat *etc*.

For simplicity, in this and all subsequent examples, the call for the script is assumed either to be aliased to or explicitly entering the current path (i.e., /usr/people/ebyrd/bin/master_densheat.s), and shall be shortened in the text, as illustrated for the previous example:

>>master_densheat.s *filename1*.dat *filename2*.dat *etc*.

If the script has not been aliased to the full path, or the full path is not used, the script will not function. Please contact CACC with aid in setting up an alias or type out the full path for each use of the script (/usr/people/ebyrd/bin/master_densheat.s).

The user can define either a density calculation or heat of formation calculation (default is to do both) using the "-d" and "-h" flags:

>>master_densheat.s –h *filename*.dat
>>master_densheat.s –d *filename*.dat

The flags that may be called are as follows:

-b --b -build --build	Only build the required Gaussian input files.
-h --h -heat --heat	Only compute the heat of formation and write data to heat_of_formation.out.
-d --d -density --density	Only compute the crystalline density and writes data to density.out.
-help	Print help page for script to screen.

The script may be run in the background (using the & command), allowing continued use of the xterm window (as well as allowing the script to run if the xterm window is closed), with standard out data printed to a file through the following command:

>>master_densheat.s *filename*.dat > *tempname* &

If the background command (&) is not used upon logging out of the xterm window, the script will terminate and not produce the final results. It is strongly recommended that the background command be used in all submissions in order to prevent re-running of the script due to the xterm window prematurely closing.

2.4 Format of the Input File

The input file (*filename*.dat) will have one of two formats—one for neutral molecules, and one for ionic molecules. The script will determine the appropriate files to construct and submit based on the data in the input file. The input files are almost completely format-free, with the only caveat that the first line must not be blank.

For neutral molecules, the first line must delineate the atom/group breakdown of the molecule, as per reference 1. This required data must be input with the following order:

C H N O C' N' O' C-NO_2 N-NO_2 O-NO_2 C-N_3 X-NO ,

with the first four (CHNO) denoting the number of unconjugated carbon, hydrogen, nitrogen, and oxygen atoms in the molecule. The following three (C'N'O') are the number of conjugated carbon, nitrogen, and oxygen atoms in the molecule. The remainder are the group-based additivity values, with the first three the number of nitro groups (NO_2) bonded to carbon, nitrogen, and oxygen, followed by the number of azido groups (N_3) bonded to carbon and the total number of nitroso moieties (NO). Using nitromethane (CH_3NO_2) as an example, this would yield as a first line to the input file:

1 3 0 0 0 1 2 1 0 0 0 0

Subsequent lines in the input file must be atom type (either atomic number or symbol (e.g., C or 6)), followed by the Cartesian coordinates in Ångströms. The number of spaces between the atom types and coordinates is not fixed (free format). Additionally, blank lines between rows will be ignored.

Similarly for ionic materials, the first line must denote first the charge of the moiety, followed by the number of times the ionic moiety appears in the total molecular complex. Subsequent lines must be atom type (either atomic number or symbol [e.g., N or 7]), followed by the Cartesian coordinates in Ångströms (once again format free and ignoring blank lines). This format is repeated for each moiety in the molecular complex. The order of the moieties within the input file is irrelevant; however, the total charge must be zero for the molecular system.

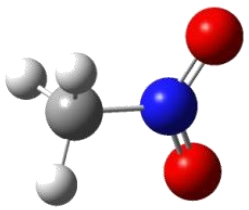
The Appendix gives a brief tutorial on the *gaussview* program, which can be used to construct Cartesian coordinates if needed.

2.5 Examples

Sample test cases with associated inputs, Gaussian outputs, and final density and heat of formation outputs are included in the /usr/people/ebyrd/bin/script_examples/ directory.

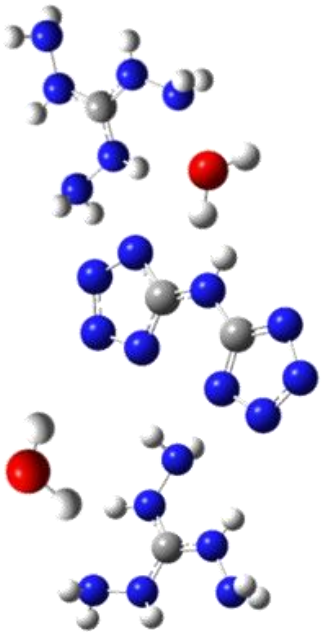
Neutral example: Nitromethane (CH_3NO_2):

1 3 0 0 0 1 2 1 0 0 0 0			
C	**-1.91299700**	**-0.32347600**	**7.60644100**
7	**-0.70935800**	**0.57063300**	**7.59458100**
O	**0.08637700**	**0.44472600**	**8.51978100**
O	**-0.62778900**	**1.38491900**	**6.68070600**
1	**-2.63104348**	**0.12211454**	**8.29868770**
1	**-2.32224168**	**-0.35240633**	**6.59826669**
H	**-1.60067525**	**-1.30351263**	**7.96292804**



Ionic example: triaminoguanidinium bis(triazolyl)amine [$(CH_9N_6^+)_2$ $(C_2 H N_9)^{2-}$ $(H_2O)_2$]:

-2 1			
N	**4.688**	**3.109**	**2.826**
7	**4.211**	**3.610**	**1.647**
N	**4.127**	**4.909**	**1.734**
N	**4.533**	**5.323**	**2.956**
N	**5.323**	**4.200**	**4.878**
N	**5.368**	**1.836**	**5.274**
N	**5.855**	**1.085**	**6.297**
N	**6.373**	**1.863**	**7.188**
7	**6.246**	**3.161**	**6.792**
C	**4.855**	**4.191**	**3.586**
6	**5.641**	**3.069**	**5.624**
H	**5.570**	**4.924**	**5.253**
0 2			
O	**7.781**	**-0.916**	**3.731**
H	**7.872**	**-1.798**	**3.449**
H	**8.121**	**-0.717**	**4.463**
1 2			
N	**3.176**	**-0.379**	**2.305**
N	**4.003**	**0.041**	**3.372**
N	**5.066**	**-1.276**	**1.348**
N	**5.645**	**-1.951**	**0.251**
N	**3.019**	**-1.562**	**0.333**
N	**1.613**	**-1.420**	**0.427**
C	**3.742**	**-1.085**	**1.334**
H	**3.416**	**-2.212**	**-0.184**
1	**1.273**	**-2.195**	**0.685**
1	**2.196**	**-0.318**	**2.304**
H	**6.301**	**-2.575**	**0.579**
1	**4.119**	**0.937**	**3.383**
H	**5.555**	**-0.738**	**1.869**
H	**3.557**	**-0.287**	**4.134**
H	**1.231**	**-1.224**	**-0.382**
H	**6.086**	**-1.279**	**-0.158**



2.6 Restrictions and Errors

Please note that there are some restrictions on the atom types capable of being handled by the various tools. For neutral materials, the heat of formation tool has only been parameterized for CHNO containing molecules. For ionic materials, while the capability exists for ionic heat of formation calculations for molecules containing hydrogen (H) through to chlorine (Cl), the tool has only been validated for CHNO materials, and is, therefore, restricted to these atoms. It is possible to expand the range of atoms for the ionic heat of formation calculation by editing the *arl_densheat.s* script, and commenting out the current **declare –a g03e0** line near the top of the script and commenting in the subsequent **declare –a g03e0** call. Meanwhile, though the density predictor tool has no inherent limitations on atom type, this tool has only been validated for CHNO-containing compounds.

Currently, the script assumes the Gaussian job will complete within 4 h using 32 processors and a ptile of 8. Additionally, the time between checking the *qstat* run queue is set to 5 min. If these values are insufficient due to the size of the calculation required (most likely due to large ionic calculations), then there exists the *large_master_densheat.s* script, which requests 96 h and 64 CPUs. If this script is insufficient, then modification of the script is required. The relevant parameters can be set at the top of a local copy of the *master_densheat.s* script. The following parameters can be modified at the top of the *master_densheat.s* script:

waittime	wait time to ping queue (default: 5 min)
nproc	number of processors for Gaussian calculation (default: 32)
ntime	queue limit for Gaussian calculation (default: 4 h)
nptile	number of cores per node (default: 8 on Harold)
nqueue	queue to use (standard, debug, challenge, background)
nproject	project account code (default: determined automatically)

Please remember to comment out any duplicates by inserting "##" at the beginning of the line.

If the Gaussian calculations terminate after successful submission with an error "died without ever signing in," this is a sign that the secure shell is corrupted in some manner. Perform the following in order to obtain a successful Gaussian completion:

Delete the $HOME/.ssh/ folder with the command
>> rm –f $HOME/.ssh/

and wait ~10–30 min for it to re-appear. Copy the following commands into the *config* file into the new $HOME/.ssh/ directory.

```
Host *
   ForwardX11 yes
   LogLevel=quiet
   Host * Banner no
   StrictHostKeyChecking no
Host *
```

ForwardX11Trusted yes
ForwardAgent yes

This should allow successful submission of future script calls to Gaussian.

---

3. Results and Discussion

Upon submission, the script will being outputting information to the screen (unless the standard output is piped to a temporary file through the > command (as denoted previously)). Additionally, up to three output files will be generated (along with a host of intermediary files). These three output files are the informational output file (*arl_densheat.err*), the heat of formation output file (*heat_of_formation.out*), and the density output file (*density.out*).

The *arl_densheat.err* file is a general message file, containing what has been done along the course of the script (e.g., files built, submitting of Gaussian jobs with associated queue information, construction of EDAT files, etc.). If the script fails for any reason, the *arl_densheat.err* file should be checked first, as it will contain information such as whether data was not copied correctly or if there were errors in the Gaussian calculations. Dependent on the nature of the error, suggestions may be offered in this file.

The *heat_of_formation.out* file lists the name as given by the *filename* (from the *filename*.dat input file), the chemical formula as determined from the input data, and the heat(s) of formation in kcal/mol. For neutral molecules, the gas, liquid, and solid phase heats of formation are computed, for both the atom (a) and group (g) based additivity methodologies. These are denoted as $H_{fg\ (a)}$, $H_{fg\ (g)}$, $H_{fl\ (a)}$, $H_{fl\ (g)}$, $H_{fs\ (a)}$, $H_{fs\ (g)}$. For ionic materials, if the compound is a 1:1 salt, two methods have been constructed to determine the solid phase heats of formation: the Jenkins and Gutowski methods (*2*). As stated above, both are volume-based methods for determination of the lattice energies, with the Gutowski method specifically refit for 1:1 salts. If the compound is any other salt, the more general Jenkins method will be the sole solid phase heat of formation listed. A sample *heat_of_formation.out* is presented here (if the text wraps to another line, please expand the width of the xterm window):

Name Chemical formula $H_{fg\ (a)}$ $H_{fg\ (g)}$ $H_{fl\ (a)}$ $H_{fl\ (g)}$ $H_{fs\ (a)}$ $H_{fs\ (g)}$ (kcal/mol)
nitromethane (C H3 N O2) -18.555 -18.579 -26.246 -26.270 -32.740 -32.764
15-DA4MeT_n ([C2 H7 N6]1+) ([N O3]1-) Ionic $H_{f(s)}$: 33.744 Ionic $H_{f(s)}$ (Gutowski): 12.016
tag2bta ([C H9 N6]1+)2 ([C2 H N9]2-) ([H2 O])2 Ionic $H_{f(s)}$: 163.398 (kcal/mol)

The *density.out* is similar to the *heat_of_formation.out* file, with the name and chemical formula listed, followed by the crystal density in grams/cubic centimeter. The output will be in this format, regardless of whether the compound is a neutral or ionic material. A sample *density.out* is presented as follows:

Name	Chemical formula	Density (g/cc)
nitromethane	(C H3 N O2)	1.424
15-DA4MeT_n	([C2 H7 N6]1+) ([N O3]1-)	1.608
tag2bta	([C H9 N6]1+)2 ([C2 H N9]2-) ([H2 O])2	1.498

4. Conclusions

Scripts have been successfully developed to ease the complex determination of the crystalline densities and heats of formation for both neutral and ionic systems. Simple, minimal information input files are the sole requirements needed to generate these important performance predictive properties. The scripts will grant the non-expert user the capability to predict, *a priori*, the crystal density and heat of formation before allocating time and resources towards synthesis. To quote a beta tester: "Prior to this script, it was very labor-intensive to be able to get the numbers from the computer. There was a series of three calculations per molecule which had to be submitted only after the previous run was complete (due to issues with trying to get Gaussian to combine the jobs this was the work around), then very long command strings and specific file formats that had to be remembered and entered correctly and in the correct sequence in order to get reasonable numbers. It would not have been possible for someone that had not been specifically trained in using the system and already had a reasonable knowledge of command based computer use (in other words old school without a GUI) to use the previous method of calculating the heat and density.

With the new script, the process is infinitely simplified with only one .dat file to build with the atomic co-ordinates and the correct functional group allocations, and the script will build all of the required files, submit the jobs, and do the after-calculation number-crunching without requiring any further input from the user.

Not only does the script drastically simplify the process, but it also cuts the required time by more than half and all but eliminates transcription errors that could have, and frequently did occur when … first learning the old system, in building the correct files for the correct job (*22*)."

5. References

1. Byrd, E.F.C.; Rice, B. M. *J. Phys. Chem. A* **2006**, *110* (3), 1005–1013; *ibid* **2009**, *113*, 5813.
2. Byrd, E.F.C.; Rice, B. M. *J. Phys. Chem. A* **2009**, *113* (1), 345–352.
3. Rice, B. M.; Hare, J. J.; Byrd, E.F.C. *J. Phys. Chem. A* **2007**, *111* (42), 10874–10879.
4. Atkins, P. W. *Physical Chemistry*; Oxford University Press: Oxford, 1982.
5. Politzer, P.; Murray, J. S.; Brinck, T.; Lane, P., in Immunoanalysis of Agrochemicals, (Nelson, J. O; Karu, A. E.; Wong, R. B., Editors), ACS Symp. Ser. 1994, 586, American Chemical Society, Washington, D.C., Chapter 8.
6. Murray, J. S.; Politzer, P. in Quantitative Treatment of Solute/Solvent Interactions, (Politzer P.; Murray, J. S., Editors), Theoretical and Computational Chemistry 1994, 1, Elsevier Scientific, Amsterdam, pp. 243-289.
7. Politzer, P.; Murray, J. S. *J. Phys. Chem. A* **1998**, *102*, 1018.
8. Murray, J. S.; Lane, P.; Politzer, P. *Mol. Phys.* **1998**, *93* (2), 187–194.
9. Rice, B. M.; Hare, J. J. *J. Phys. Chem. A* **2002**, *106*, 1770.
10. Murray, J. S.; Lane, P.; Politzer, P. *Mol. Phys.* **1995**, *85* (1), 1–8.
11. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627
12. (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (b) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265. (c) Clark, T.; Chandrasekhar, J.; Schleyer, P.V.R. *J. Comp. Chem.* **1983**, *4*, 294.

13. Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

14. Jenkins, H.D.B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609

15. Jenkins, H.D.B; Liebman, J. F. *Inorg. Chem.* **2005**, *44*, 6359.

16. Jenkins, H.D.B.; Glasser, L.; Klapötke, T. M.; Crawford, M.-J.; Bhasin; Lee, J.; Schrobilgen, G. J.; Sunderlin, L. S.; Liebman, J. F. *Inorg. Chem.* **2004**, *43*, 6238.

17. Jenkins, H.D.B. *J. Chem. Ed.*, **2005**, *82*, 950.

18. Jenkins, H.D.B.; Tudela, D.; Glasser, L. *Inorg. Chem*., **2002**, *41*, 2364.

19. Jenkins, H.D.B.; Glasser, L. *Inorg. Chem.*, **2006**, *45*, 1754.

20. Gutowski, K. E.; Rogers, R. D.; Dixon, D. A. *J. Phys. Chem. B*, **2007**, *111*, 4788.

21. Baboul, A. G.; Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. Gaussian-3 Theory Using Density Functional Geometries and Zero-point Energies. *J. Chem. Phys.*, *110* (1999) 7650–57.

22. Private communication with William Sherrill, ARL, (2012).

INTENTIONALLY LEFT BLANK.

Appendix. Supplemental Figures and Instructions for Use of *kinit, PuTTY,* and *gaussview*

Several steps are required prior to running the ARL scripts, such as gaining access to the HPC machines, logging into the HPC machines, and building the Cartesian coordinates. This appendix provides a quick guide for these required steps, but is not intended to be exhaustive. Please contact the local help desk or CCAC for assistance if further guidance is required.

Prior to logging into the HPC center, a Kerberos ticket is required, as this ensures secured communication between the local computer and the HPC supercomputer center. Running the *kinit* software will open a window similar to figure A-1 (note that for a completely new session all boxes will be blank). Under the "name" box, please enter the log-in name provided from the Consolidated Customer Assistance Center (CCAC) and enter under the "realm" box the text seen below (as of April 2012). Click on "Login" and follow the rest of the instructions. If successful, a green ticket should appear (as seen in figure A-1). If not, please contact CCAC.

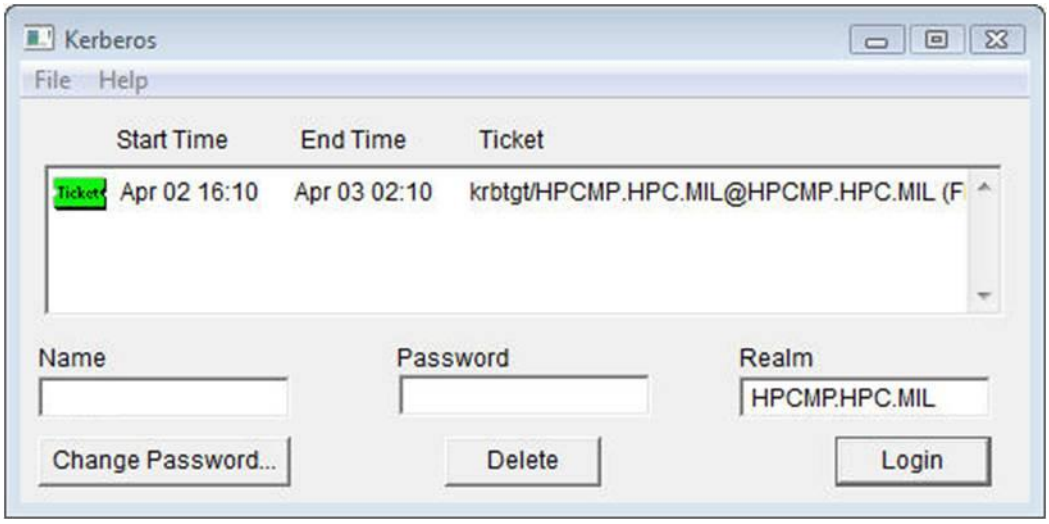


Figure A-1. Kerberos *kinit* window to obtain ticket required for access to HPC computers.

Once a Kerberos ticket has been obtained, an xterm window is required to connect to the HPC center. Open the *PuTTY* software (figure A-2) and on the "Host Name" box, enter the Harold address (harold.arl.hpc.mil", and under "saved sessions" enter the name you wish to call that session, then hit save. Henceforth, one can open a connect to that node either by double clicking on the saved session or clicking on the saved session, clicking on "load," and, finally, clicking on "open" in the bottom right.

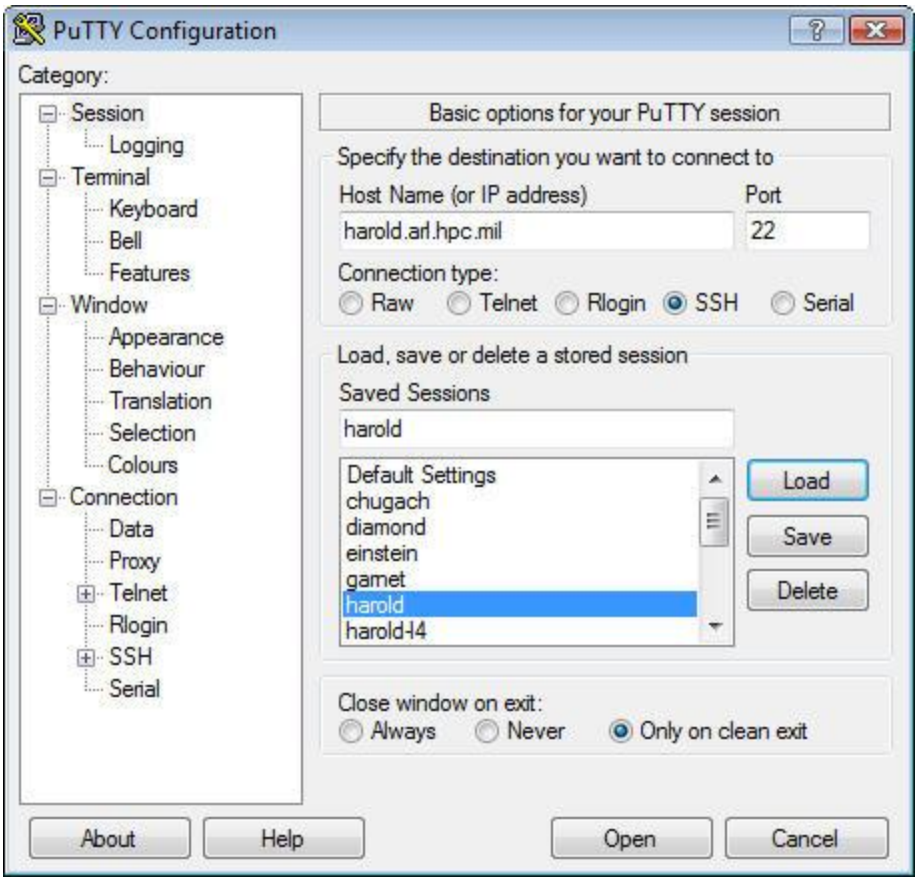


Figure A-2. *PuTTY* window to open connection to HPC computers.

In order to interface with a graphical user interface (GUI), the local machine must be hosting an xserver emulator. If not, the HPC machines will not be able to transfer the graphics successfully to the local machine. Two common xserver emulators are *Exceed3D* and *Cygwin-X*. Please contact the local help desk for installation of either of the xserver emulators to the local machine and ensure that the xserver portion of the software is installed (for example, for *Cygwin-X*, the *XWin Server* is the required portion of the software). Once installed, double-click on the xserver and leave it running in the background prior to using any HPC-hosted GUI. As stated, failure to have an xserver running in the background on the local machine will cause the HPC-hosted GUI to fail.

Once access to the Gaussian program package has been obtained (means to test access in main text), access to the *gaussview* program is also granted. This tool is a graphical interface for building and visualizing molecular systems. The online reference manual can be found here: http://www.gaussian.com/g_tech/gv5ref/gv5ref_toc.htm; and the brochure can be found here: http://www.gaussian.com/g_prod/gv5b.htm. To run *gaussview* at the prompt (denoted ">>" in the text), type the following commands:

>>gview

If the xserver emulator is running properly, figure A-3 should appear on the local machine screen. Please refer to the reference manual for an in-depth tutorial and guidance on usage.

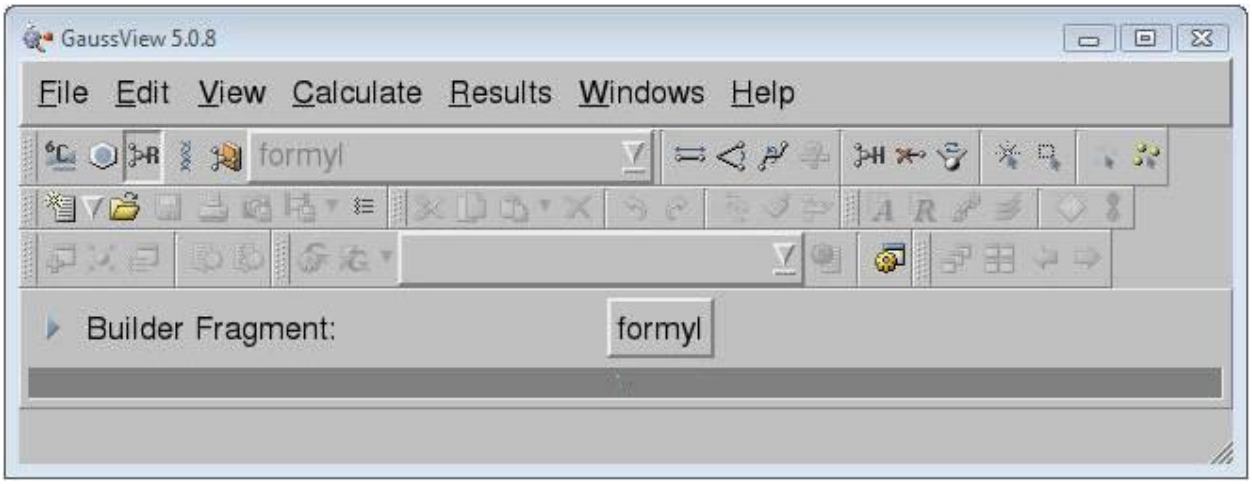


Figure A-3. *Gaussview* main window.

For construction of molecular systems (needed to obtain the *xyz* Cartesian coordinates required for the *.dat* input file for the script), three buttons will be used most frequently: the element builder (figure A-4), the ring builder (figure A-5), and the R-group builder (figure A-6). Clicking on a button will open the appropriate builder.

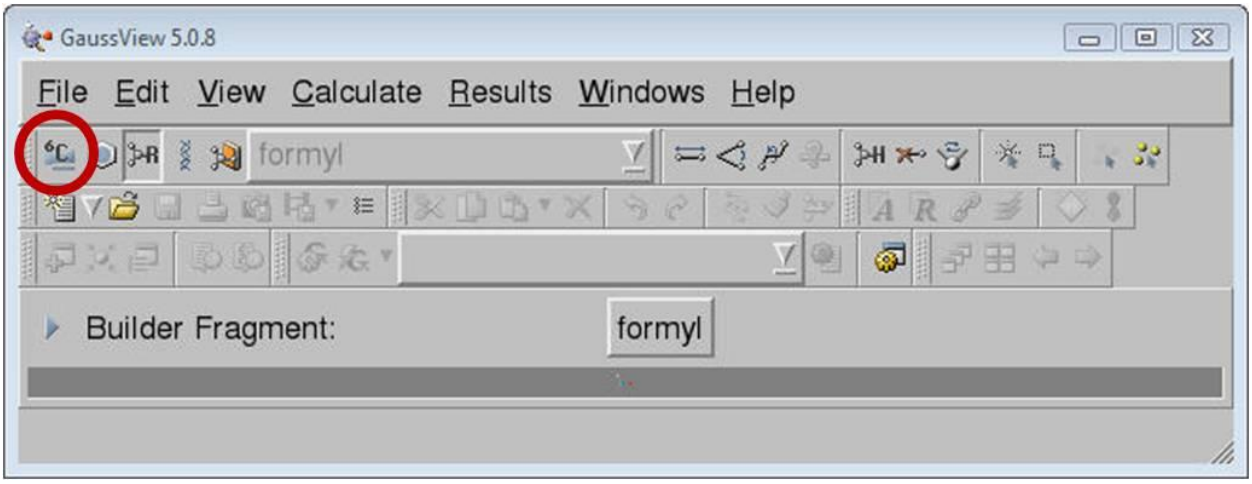


Figure A-4. Button to select for access to the element fragment builder in *gaussview.*

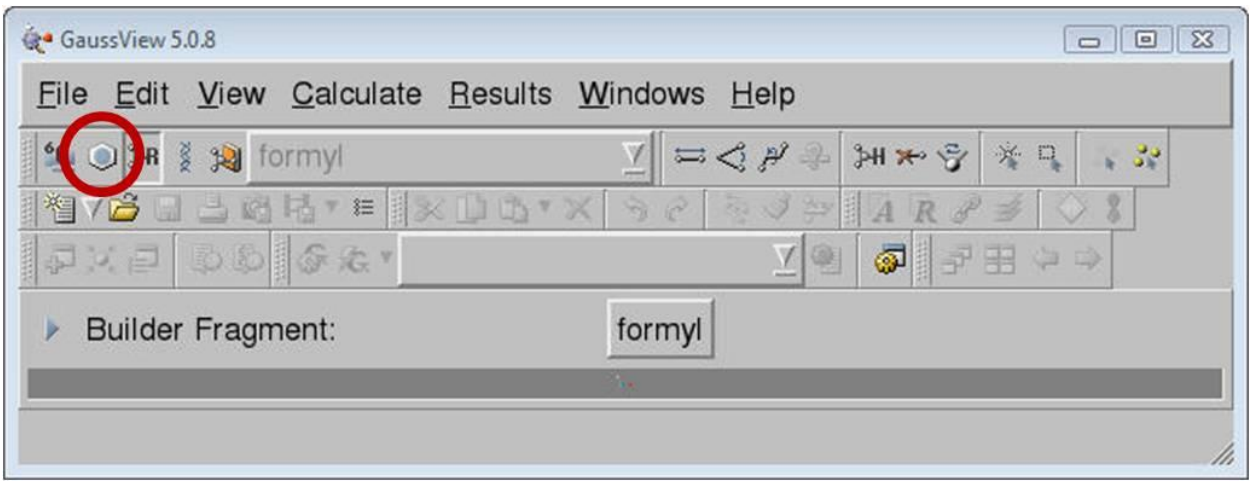


Figure A-5. Button to select for access to the ring fragment builder in *gaussview*.

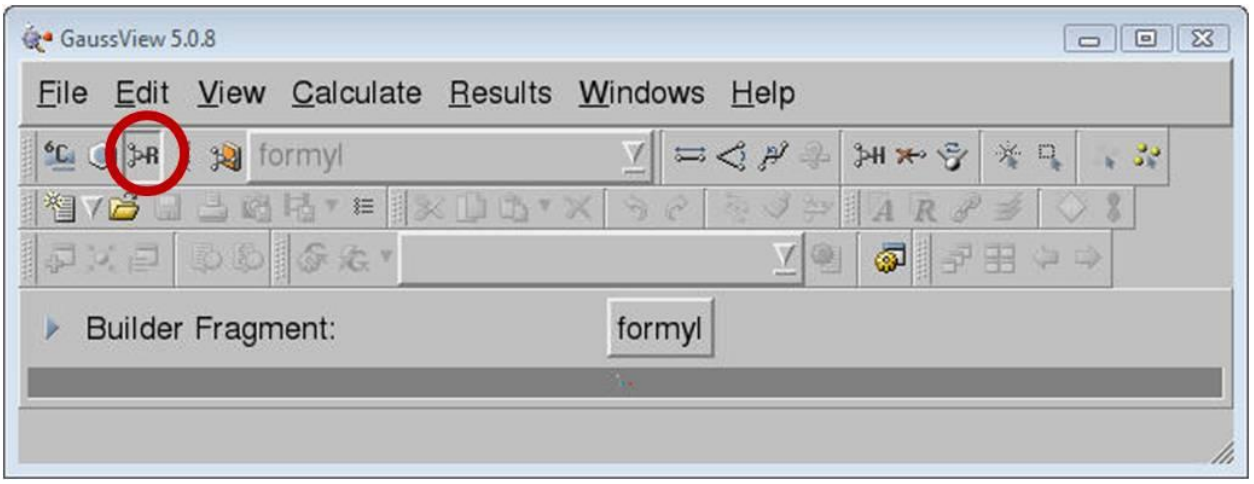


Figure A-6. Button to select for access to the R-Group fragment builder in *gaussview*.

The elemental fragment builder (figure A-7) can be used to add individual atoms or change existent atoms into different ones. Select the desired atom and valency (bonding type), and then click on the molecule window. If the mouse is placed and clicked in a void region, the selected atom will be added and capped with hydrogens. If the mouse is over an existent atom and then clicked, that atom will be replaced by the current selection from the element fragment builder.

Hint: The bonds displayed in the molecular viewing window do not indicate actual bonds, as they are rendered solely on atom-atom bond distances. *Gaussview* has no knowledge of the electronic structure (and, thus, the bonds) and is only displaying an estimate of the bonding structure.

Hint: If one wants to merely replace an existent atom with another without changing the current bonding, when selecting the bonding type (bottom of the element fragment builder), select the "Atom" (far left) designation; this will not alter any existing bonds.

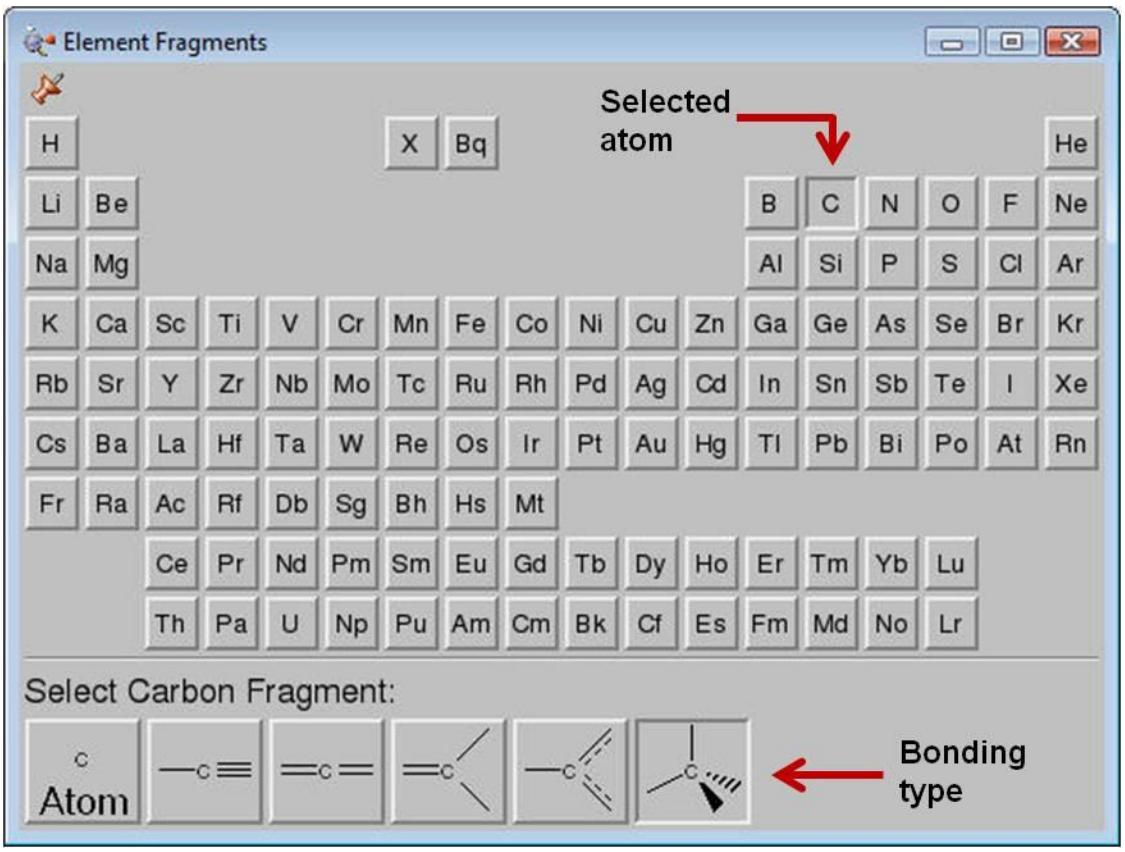


Figure A-7. Element fragment builder in *gaussview*.

Gaussview has included a library of common ring (figure A-8) and functional groups (figure A-9), which can be added in a similar manner as an element. Selecting a fragment and clicking on a void space in the molecule window will add that fragment and terminate any required bonds with hydrogens. Clicking on an existing atom will replace that atom with the selected group.

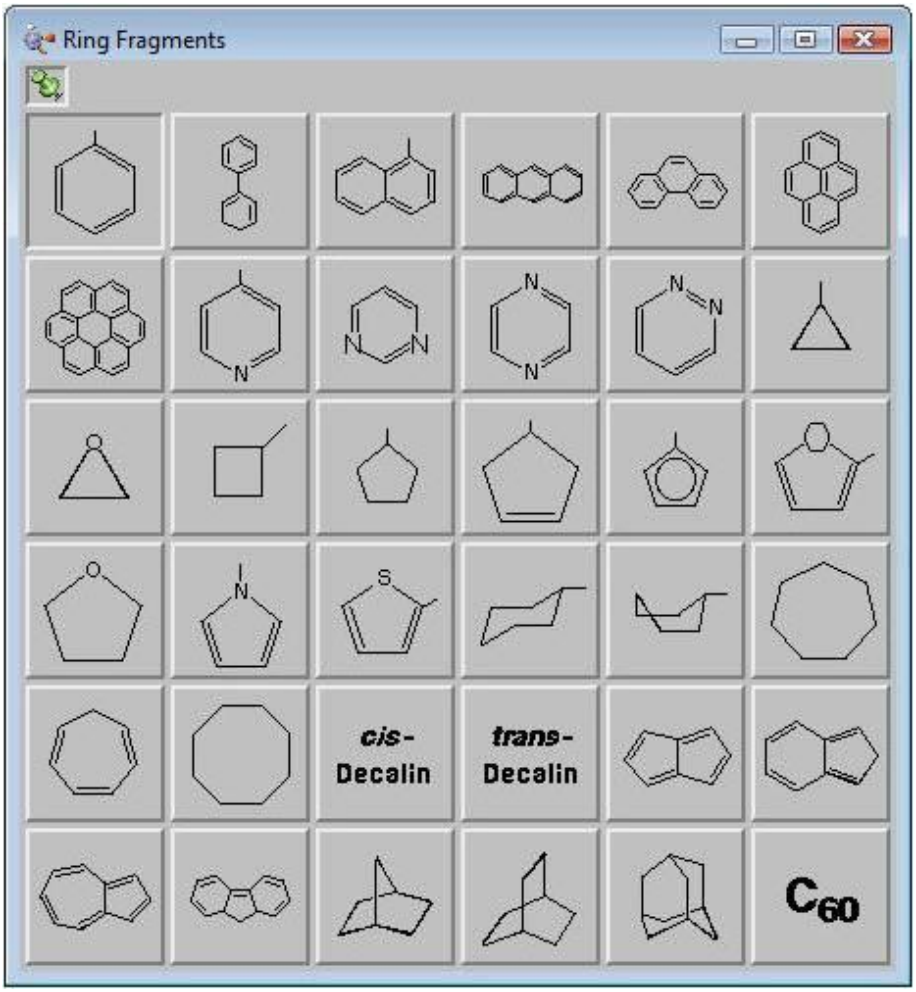


Figure A-8. Ring fragment builder in *gaussview*.

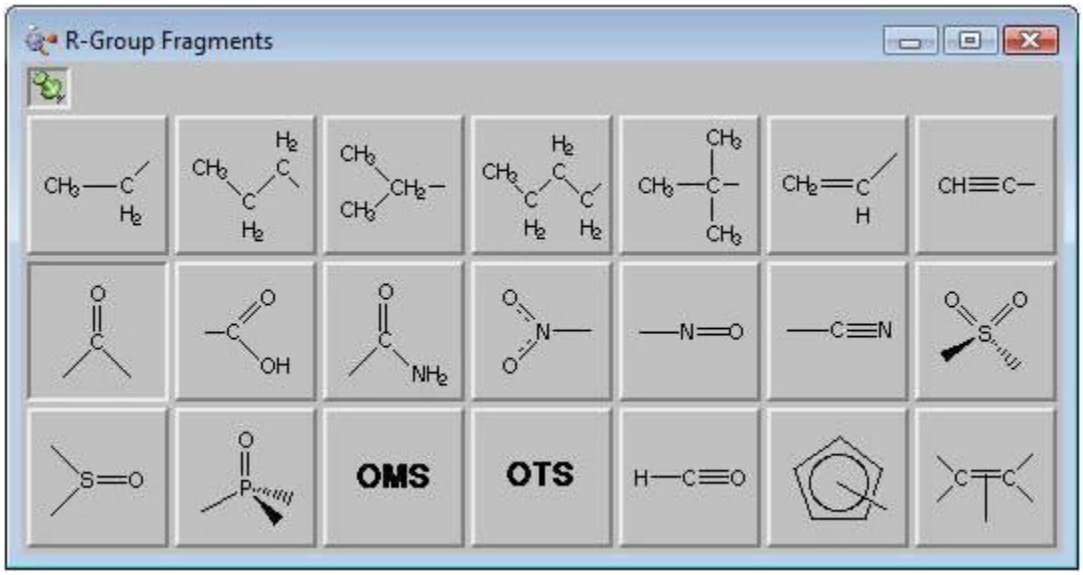


Figure A-9. R-Group fragment builder in *gaussview*.

Once the general molecular geometry has been constructed, modification of the bond lengths, angles, and dihedrals is possible (figure A-10). Once selected, a pop-up box will appear, allowing the relevant atoms or groups to move or be frozen.

Hint: A common issue with geometry optimizations (as performed by the script) is the occurrence of imaginary frequencies (i.e., maxima on the potential energy surface instead of minima). A vast majority of the time, this can be avoided by assuring that there are no angles equal to **exactly** 90° and no dihedrals equal to **exactly** 180°. For technical reasons, structures containing these angles and dihedrals usually do not perform the proper gradient-directed steps required to optimize the geometry to a minima structure. Breaking these symmetries *very* slightly (e.g., 90.05° versus 90°) is all that is required in order to obtain a reasonable optimized structure that still has the desired structure (to within the accuracy of the theory).

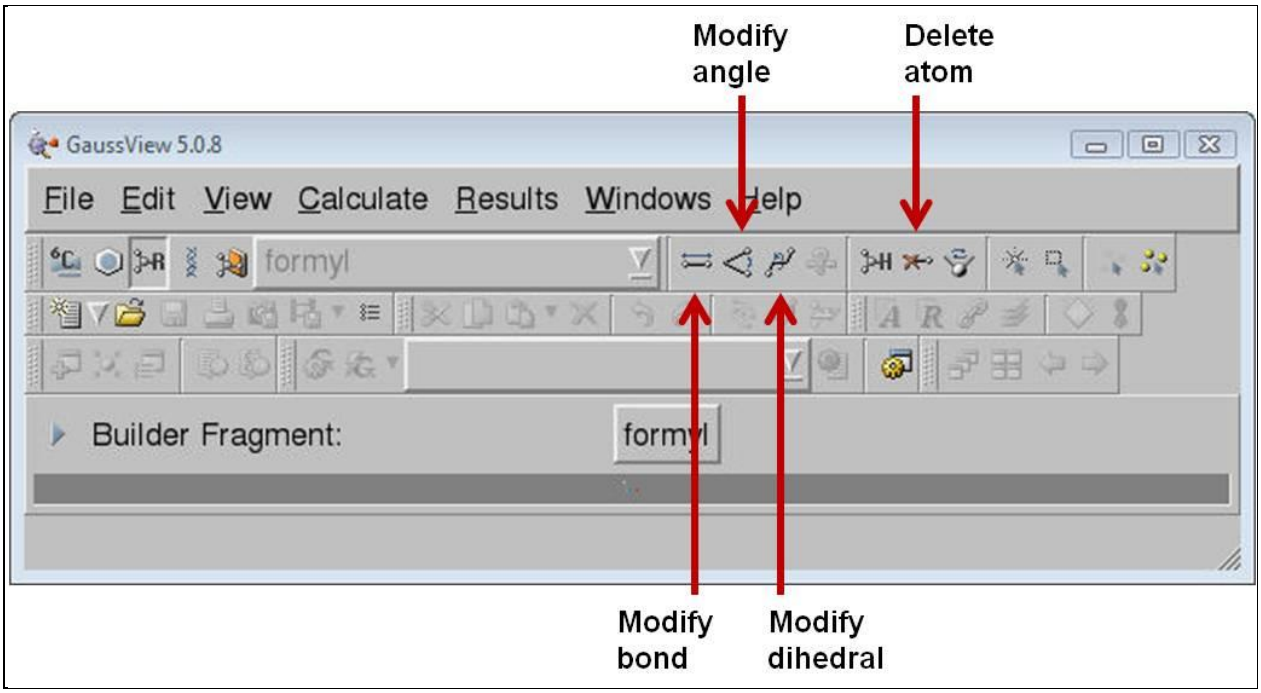


Figure A-10. Options to modify structures.

Once the final desired structure has been constructed, it is necessary to save the geometry for transcription to the *.dat* script input file. Figure A-11 is the menu displayed when saving a file in *gaussview*. It is advised to have "Save as:" set to "Gaussian Input File" versus "Auto." Once the "Save as:" has been changed, be certain to select "Write Cartesians" in the lower left. Type an appropriate file name and hit "Save."

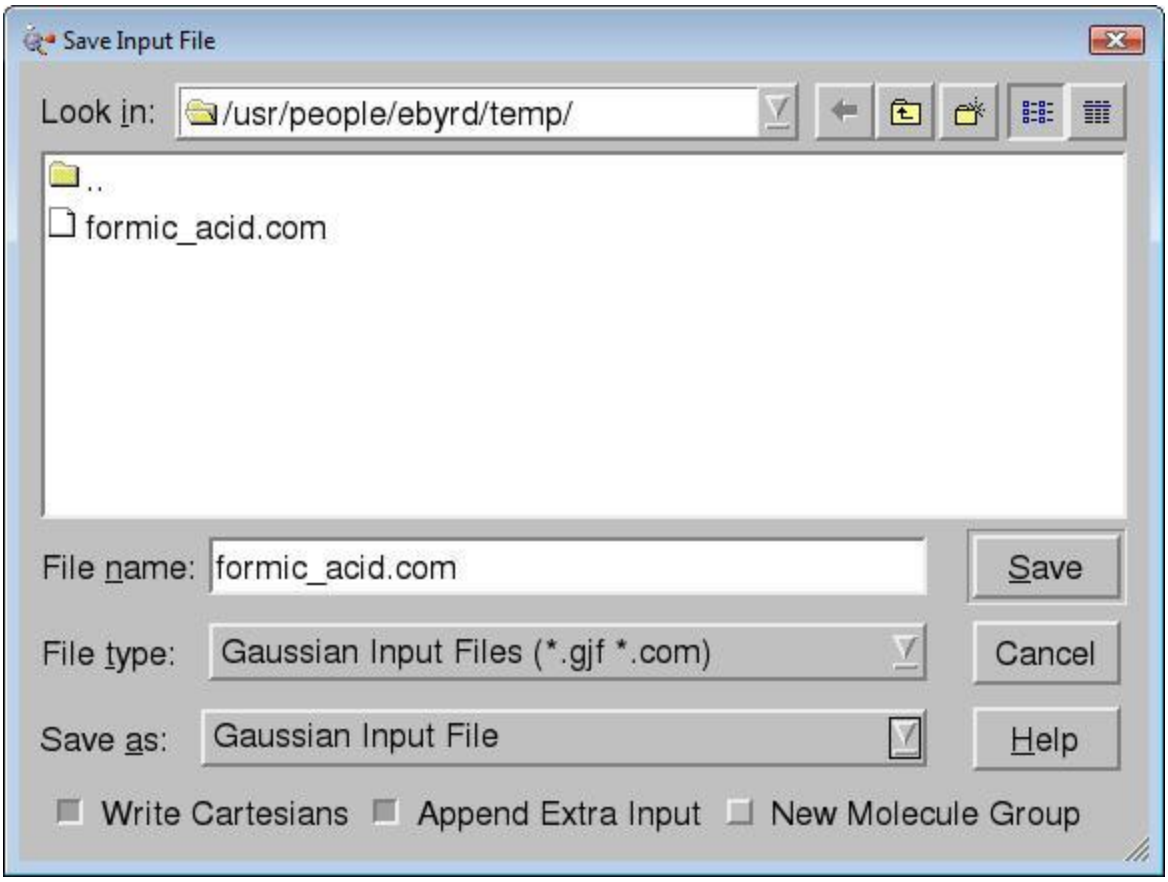


Figure A-11. *Gaussview* save menu.

Using one of the UNIX-supplied text editors (e.g. *vi*, *emacs*), open the saved *.com* file (example illustrated in figure A-12) and select the atomic coordinates and paste them into the appropriate *.dat* file.

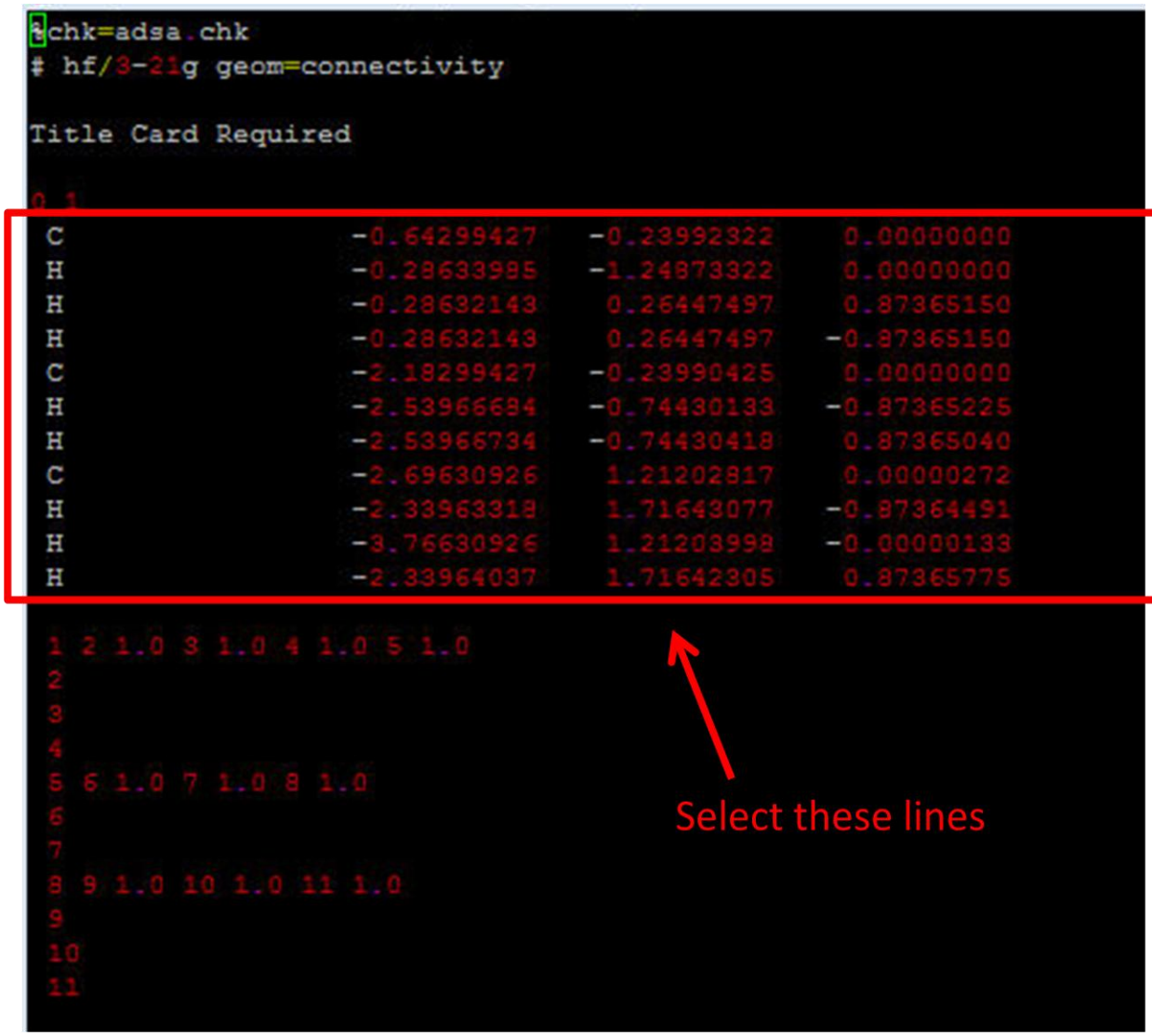


Figure A-12. Saved Gaussian09 input file.

Hint: Recall that for ionic compounds, each individual subunit of the complex is separate from the other. Either build and save each subunit separately (and paste into the *.dat* file), or build the entire system and edit the *.com* file appropriately (i.e., delete all data in *.com* file except for the atoms and coordinates and use the "View, Labels" menu option in *gaussview* to group atoms into the correct molecular subunit). Please refer to online manuals for detailed instructions on the use of *vi* and/or *emacs*.

INTENTIONALLY LEFT BLANK.

List of Symbols, Abbreviations, and Acronyms

6-31G*	Pople's Gaussian double-zeta polarized basis set with *d* polarization functions on each of the atoms Li through Ca
6-31G**	Pople's Gaussian double-zeta polarized basis set with *d* polarization functions on each of the atoms Li through Ca and *p* polarization functions on H and He
6-311++G(2df,2p)	Pople's Gaussian triple-zeta polarized basis set with 2*d* and *f* polarization functions on each of the atoms Li through Ca and 2*p* polarization functions on H and He along with *s* and *p* diffuse functions on each of the atoms Li through F and *s* diffuse functions on H and He
Å	Ångström
ν	Balance parameter
Σ	Average electrostatic surface potential
σ^2	Variance of electrostatic surface potential
p	Electronic density
$p_{crystal}$	Crystalline density
$\Delta H°_{f\,(g)}$	gas phase heat of formation
$\Delta H°_{f\,(l)}$	liquid phase heat of formation
$\Delta H°_{f\,(s)}$	solid phase heat of formation
$\Delta H°_{Lattice}$	Lattice enthalpy
C	Carbon
C'	Carbon with hybridization
H	Hydrogen
N	Nitrogen
N'	Nitrogen with hybridization

N_3	Azide group
NO_2	Nitro group
O	Oxygen
O’	Oxygen with hybridization
R^2	Coefficient of determination
U_{pot}	Lattice potential energy
V	Electrostatic potential
X	Unknown/unassigned atom type
ARL	U.S. Army Research Laboratory
B3LYP	Becke 3 parameter exchange with Lee-Yang-Parr correlation DFT functional
CCAC	Consolidated Customer Assistance Center
CPU	Central processing unit
DFT	Density functional theory
EM	Energetic Materials
ESP	Electrostatic surface potential
G3MP2(B3LYP)	G3 variant which uses MP2 instead of MP4 for the basis set extension corrections and uses the B3LYP structures and frequencies instead of the Hartree-Fock values
g/cc	grams per cubic centimeter
GUI	graphical user interface
HPC	high performance computing
kcal/mol	Kilocalories per mole (unit of energy)
KS-DFT	Kohn-Sham density functional theory
rms	root mean square error

NO. OF COPIES	ORGANIZATION
1 ELEC	ADMNSTR DEFNS TECHL INFO CTR ATTN DTIC OCP 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
1	DARPA ATTN J GOLDWASSER 3701 NORTH FAIRFAX DR ARLINGTON VA 22203-1714
1	DTRA ATTN B WILSON 8725 JOHN J KINGMAN RD MS 6201 FT BELVOIR VA 22060-6201
1	CDR US ARMY TACOM ARDEC ATTN AMSRD AR AEM C J MURNANE BLDG 61S PICATINNY ARSENAL NJ 0706-5000
1	CDR US ARMY TACOM ARDEC ATTN RDAR MEF E T RECCHIA BLDG 94 PICATINNY ARSENAL NJ 0706-5000
3	CDR US ARMY TACOM ARDEC ATTN RDAR MEF I J CHOI ATTN RDAR MEF I L VO ATTN RDAR MEF I R GRANITZKI BLDG 95 PICATINNY ARSENAL NJ 0706-5000
7	CDR US ARMY TACOM ARDEC ATTN RDAR MEF S B DEFRANCO ATTN RDAR MEF S D PANHORST ATTN RDAR MEF S D PASCUA ATTN RDAR MEF S G MINER ATTN RDAR MEF S M MARSH ATTN RDAR MEF S N GRAY ATTN RDAR MEF S P FERLAZZO BLDG 94 PICATINNY ARSENAL NJ 0706-5000
3	CDR US ARMY TACOM ARDEC ATTN RDAR MEM A E VAZQUEZ ATTN RDAR MEM A S CHUNG ATTN RDAR MEM A W KOENIG BLDG 94S PICATINNY ARSENAL NJ 0706-5000
1	CDR US ARMY TACOM ARDEC ATTN SFAE AMO CAS P MANZ BLDG 172 PICATINNY ARSENAL NJ 0706-5000
1	CDR US ARMY TACOM ARDEC ATTN SFAE AMO CAS R KIEBLER BLDG 171A PICATINNY ARSENAL NJ 0706-5000
1	CDR US ARMY TACOM ARDEC ATTN SFAE AMO MAS C GRASSANO BLDG 354 PICATINNY ARSENAL NJ 07806-5000
1	CDR US ARMY TACOM ARDEC ATTN V MATRISCIANO BLDG 151 JLW PICATINNY ARSENAL NJ 07806-5000
1	OFC OF THE PROD MGR FOR EXCALIBUR ATTN SFAE AMO CAS EX M BURKE BLDG 171 PICATINNY ARSENAL NJ 07806-5000
1	OPM MANEUVER AMMUNITION SYSTEMS ATTN SFAE AMO MAS SMC R KOWALSKI BLDG 354 PICATINNY ARSENAL NJ 07806-5000
2	OPM MANUEVER AMMUNITION SYSTEMS ATTN SFAE AMO MAS SMC J LUCID ATTN SFAE AMO MAS SMC P RIGGS BLDG 354 PICATINNY ARSENAL NJ 07806-5000
2	PM ARMS ATTN SFAE AMO MAS SMC H KOURLOS ATTN SFAE AMO MAS SMC K THOMAS BLDG 354 PICATINNY ARSENAL NJ 07806-5000

NO. OF COPIES	ORGANIZATION
1	PM MAS ATTN SFAE AMO MAS SETI J FOULTZ BLDG 354 PICATINNY ARSENAL NJ 07806
1	RDECOM ARDEC ATTN RDAR MEM A J GRAU BLDG 94 PICATINNY ARSENAL NJ 07806-5000
2	RSRCH DEV TEST AND EVAL INDIAN HEAD DIV NSWC (IHDIV NSWC) ATTN CODE R22LN L A NOCK ATTN CODE R22MS1 M H SHERLOCK 4103 FOWLER RD STE 205 BLDG 302 INDIAN HEAD MD 20640-5106
1	US ARDEC ATTN RDAR MEF M HOHIL BLDG 407 PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARDEC ATTN RDAR MEE T J SABATINI BLDG 1515 PICATINNY ARSENAL NJ 07806
1	US ARMY ARDEC ATTN AMSRD AAR AEM T M NICOLICH BLDG 65S PICATINNY ARSENAL NJ 07806-5000
2	US ARMY ARDEC ATTN AMSRD AAR EI R CARR ATTN AMSTA AAR AEM I M VOLKMANN BLDG 65N PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARDEC ATTN RDAR MEE W A DANIELS BLDG 3022 PICATINNY ARSENAL NJ 07806-5000
3	US ARMY ARDEC ATTN RDAR MEE W E CARAVACA ATTN RDAR MEE W J O'REILLY ATTN RDAR MEE W P ANDERSON BLDG 382 PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARDEC ATTN RDAR MEE W R DAMAVARAPU BLDG 2028 PICATINNY ARSENAL NJ 07806-5000
2	US ARMY ARDEC ATTN RDAR MEE W R SURAPANENI ATTN RDAR MEE W S NICOLICH BLDG 3022 PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARDEC ATTN RDAR MEE W W BALAS-HUMMERS BLDG 382 PICATINNY ARSENAL NJ 07806-5000
6	US ARMY ARDEC ATTN RDAR MEF E A SANCHEZ ATTN RDAR MEF E C STOUT ATTN RDAR MEF E D CARLUCCI ATTN RDAR MEF E R HOOKE ATTN RDAR MEM C A LICHTENBERG-SCALON ATTN RDAR MEM C D DEMELLA BLDG 94 PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARDEC ATTN RDAR MEM C M LUCIANO BLDG 65S PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARDEC ATTN RDAR MEM C P MAGNOTTI BLDG 94 PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARDEC ATTN RDAR MEM C P SAMUELS BLDG 172 PICATINNY ARSENAL NJ 07806-5000

NO. OF COPIES	ORGANIZATION
1	US ARMY ARDEC ATTN RDAR QES C M WESSEL BLDG 62 PICATINNY ARSENAL NJ 07806-5000
2	US ARMY ARDEC ATTN RDRL MEM E LOGSDON ATTN RDRL MEM R SAYER BLDG 65 PICATINNY ARSENAL NJ 07806-5000
2	US ARMY ARDEC ATTN SFAE AMO CAS MS G SCHWARTZ ATTN SFAE AMO CAS MS P BURKE BLDG 162S PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARDEC ATTN SFAE SMO MAS LC T D RIGOGLIOSO BLDG 354 PICATINNY ARSENAL NJ 07806-5000
1	US ARMY ARMAMENT RD&E CENTER ATTN RDAR MEM C D NGUYEN BLDG 94 PICATINNY ARSENAL NJ 07806-5000
2	US ARMY AVIATION & MISSILE COMMAND ATTN AMSRD AMR PS PT J LILLY ATTN AMSRD AMR PS PT R MICHAELS BLDG 7120 REDSTONE ARSENAL AL 35898-5249
2	US ARMY AVN & MIS CMND ATTN AMSRD AMR PS PT L PLEDGER ATTN AMSRD AMR PS PT M MORRISON BLDG 7120 REDSTONE ARSENAL AL 35898
2	US ARMY AVN & MIS CMND ATTN AMSRD ARL PS PT G DRAKE ATTN AMSRD ARL PS PT N MATHIS BLDG 7120 REDSTONE RD REDSTONE ARSENAL AL 45898

NO. OF COPIES	ORGANIZATION
1	US ARMY RDECOM ATTN RDMR WDN P JOHNS 7120 REDSTONE RD REDSTONE ARSENAL AL 35898
1	US ARMY RDECOM ARDEC ATTN RDAR MEM A G MALEJKO BLDG 94S PICATINNY ARSENAL NJ 07806-5000
1	US ARMY TACOM ARDEC ATTN RDAR MEE W J LONGCORE BLDG 382 PICATINNY ARSENAL NJ 07806-5000
2	COMMANDER US ARMY TACOM ARDEC ATTN RDAR MEF S R FULLERTON ATTN RDAR MEM M C MOEHRINGER BLDG 94 PICATINNY ARSENAL NJ 07806-5000
4	US ARMY TACOM-ARDEC ATTN RDAR MEE W A DAWSON ATTN RDAR MEE W E BAKER ATTN RDAR MEE W L COSTAS ATTN RDAR MEE W W DAVIS BLDG 3022 PICATINNY ARSENAL NJ 07806-5000
4	US ARMY TACOM-ARDEC ATTN RDAR MEF E M S HOLLIS ATTN RDAR MEM C D CIMORELLI ATTN RDAR MEM C K SANTAGELO ATTN RDAR MEM C R GORMAN BLDG 94 PICATINNY ARSENAL NJ 07806-5000
1	USINSOM ATTN S STERBLING FT BELVOIR VA 22060-6218
1	WEAPONS DEV & INTEGRATION DIR ATTN RDMR WDN J B NEIDERT 7120 REDSTONE RD REDSTONE ARSENAL AL 35898
1	NAV RSRCH LAB ATTN TECHL LIB WASHINGTON DC 20375-5000

NO. OF COPIES	ORGANIZATION
2	NAVAL AIR WARFARE CTR ATTN CODE 474100D A MERRITT ATTN CODE 474100D M MASON 2400 E PILOT PLANT RD MS 5202 CHINA LAKE CA 93555
2	NAVAL AIR WARFARE CTR ATTN CODE 470000D A ATWOOD ATTN CODE 470000D S BLASHILL 2400 E PILOT PLANT ROAD, STOP 5001 CHINA LAKE CA 93555-6107
2	NAVAL AIR WARFARE CTR NAV AIR WEAPONS DIV ATTN CODE 4T4200D R CHAPMAN ATTN CODE 4T4320D T PARR 1 ADMINISTRATION CIRCLE CHINA LAKE CA 93555-6100
1	NAVAL SURF WARFARE CTR ATTN A STERN 3824 STRAUSS AVE STE 107 INDIAN HEAD MD 20640
1	NAVAL SURFACE WARFARE CTR RSRCH, DEV, TEST, AND EVAL IHDIV ATTN C MICHIENZI 4081 N JACKSON RD RM 18 INDIAN HEAD MD 20640-5116
2	NSWC DAHLGREN G33 PRECISION AND ADVANCED SYS BR ATTN L STEELMAN ATTN N COOK 6210 TISDALE RD STE 223 DAHLGREN VA 22448-5114
1	NVL SUR WARFARE CNTR ATTN H HAYDEN 4081 N JACKSON RD RM 18 INDIAN HEAD MD 20640-5116
1	OFC OF NAV RSRCH ATTN B ALMQUIST 875 N RANDOLPH ST RM 653 ARLINGTON VA 22203-1927
1	OFFICE OF NAVAL RSCH ATTN C BEDFORD 875 N RANDOLPH ST RM 653 ARLINGTON VA 22203-1927
1	AIR FORCE RSRCH LAB ATTN RWME T KRAWIETZ 2306 PERIMETER RD EGLIN AFB FL 32542
1	AIR FORCE RSRCH LAB ATTN J ZABINSKI AFRL/RXB B654 RM 135 2941 HOBSON WAY WRIGHT PATTERSON AFB OH 45433-7750
1	LAWRENCE LIVERMORE NATL LAB PHYS AND LIFE SCI DIRCTRT ATTN P PAGORIA LIVERMORE CA 94550
1	LOS ALAMOS NATL LAB ATTN L PERRY PO BOX 1663 MAIL STOP C290 LOS ALAMOS NM 87545
2	LOS ALAMOS NATL LAB DYN ENERG MATS DIV ATTN D CHAVEZ ATTN P LEONARD LOS ALAMOS NM 87545
1	US ARMY RSRCH LAB ATTN RDRL WML A F DE LUCIA ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML B J GOTTFRIED BLDG 1101 ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WM P PLOSTINS BLDG 4600 ABERDEEN PROVING GROUND MD 21005

NO. OF COPIES	ORGANIZATION
1	US ARMY RSRCH LAB ATTN RDRL WML A C MUNSON ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML B B HOMAN BLDG 4600 ABERDEEN PROVING GROUND MD 21005
11	US ARMY RSRCH LAB ATTN RDRL WML B B RICE ATTN RDRL WML B E BYRD (10 HCS) ABERDEEN PROVING GROUND MD 21005
3	US ARMY RSRCH LAB ATTN RDRL WML B I BATYREV ATTN RDRL WML B J MORRIS ATTN RDRL WML B R PESCE-RODRIGUEZ BLDG 4600 ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML B R SAUSA ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML B S BUNTE BLDG 4600 ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML B W D MATTSON ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML C G SUTHERLAND BLDG 1185 ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML C M BISS ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML C S AUBERT BLDG 1119B ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML C V BOYLE BLDG 1185 ABERDEEN PROVING GROUND MD 21005
2	US ARMY RSRCH LAB ATTN RDRL WML D J RITTER ATTN RDRL WML D R A BEYER BLDG 390 ABERDEEN PROVING GROUND MD 21005
2	US ARMY RSRCH LAB ATTN RDRL WML E P WEINACHT ATTN RDRL WML G W DRYSDALE BLDG 4600 ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML H M FERMEN-COKER BLDG 309 ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML J NEWILL BLDG 390 ABERDEEN PROVING GROUND MD 21005
2	US ARMY RSRCH LAB ATTN RDRL WML M J ZOLTOSKI ATTN RDRL WMM J ZABINSKI BLDG 4600 ABERDEEN PROVING GROUND MD 21005

NO. OF COPIES	ORGANIZATION
1	US ARMY RSRCH LAB ATTN RDRL WMP A B RINGERS BLDG 1116A ABERDEEN PROVING GROUND MD 21005
2	US ARMY RSRCH LAB ATTN RDRL WMP G R EHLERS ATTN RDRL WMP P J BAKER BLDG 309 ABERDEEN PROVING GROUND MD 21005
1	US ARMY RSRCH LAB ATTN RDRL WML D M NUSCA BLDG 390 ABERDEEN PROVING GROUND MD 21005-5056
1	US ARMY RSRCH LAB ATTN RDRL WML B J CIEZAK-JENKINS BLDG 390 ABERDEEN PROVING GROUND MD 21005-5059
1	US ARMY RSRCH LAB ATTN RDRL WM B FORCH BLDG 4600 ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML B N TRIVEDI BLDG 207 ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML C B ROOS BLDG 1119B ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML C K L MCNESBY BLDG 1185 ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML C K SPANGLER BLDG 1119B ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML C T PIEHLER BLDG 309 ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML C W SHERRILL BLDG 1119B ABERDEEN PROVING GROUND MD 21005-5066
2	US ARMY RSRCH LAB ATTN RDRL WML F D HEPNER ATTN RDRL WML F D LYON BLDG 4600 ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML F E BUKOWSKI BLDG 1119B ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML H T G BROWN BLDG 4600 ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WMP G S KUKUCK BLDG 309 ABERDEEN PROVING GROUND MD 21005-5066
1	US ARMY RSRCH LAB ATTN RDRL WML A W OBERLE BLDG 390 ABERDEEN PROVING GROUND MD 21005-5067

NO. OF
COPIES ORGANIZATION

1 US ARMY RSRCH LAB
ATTN RDRL ROP R ANTHENIEN
PO BOX 12211
RESEARCH TRIANGLE PARK NC
27709-2211

1 US ARMY RSRCH OFC
ATTN RDRL ROP C J PARKER
PO BOX 12211
RESEARCH TRIANGLE PARK NC
27709-2211

1 US ARMY RSRCH OFC
ATTN RDRL ROE V R HARMON
PO BOX 12211
RESEARCH TRIANGLE PARK NC
27709-2211

4 US ARMY RSRCH LAB
ATTN IMAL HRA
MAIL & RECORDS MGMT
ATTN RDRL CIO LL TECHL LIB
ATTN RDRL CIO LT TECHL PUB
ATTN RDRL D V WEISS
ADELPHI MD 20783-1197

INTENTIONALLY LEFT BLANK.